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Catalytic Hydrogenation Of Unsaturated Compounds.

CATALYTIC HYDROGENATION OF UNSATURATED COMPOUNDS

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY HAROLD ALVIN LEVEY

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Table of Contents.

	Page
1. Introduction	1
11. History	4
111.Theory	
General	9
Forms of Reduction	10
Relative Difficulty of Hydrogen Addition	10
Phases of Material Hydrogenated	11
Catalysers	
Forms of Catalysers	12
Relative Advantages	13
Action of Catalysers	14
Carriers	16
Relation of Occlusion to Catalysis	17
1V. Experimentation.	
Apparatus	19
Small Apparatus	19
Large Apparatus	19
Hydrogen Supply	20
Hydrogenating Apparatus	22
Construction of Apparatus	22
Distilling Flask	22
Construction of small Converter	23
Hydrogenation	26
Construction of Large Apparatus	26
Operation	
Method 1	28

UIUC

Method 11 29

Method 111 29

Preliminary Treatment of the Oil 29

Gas Piping System 29

Electrical Heating System 30

Removal Container for Catalytic Material 30

Catalysers 31

Preparation 31

Activation 32

Experiment 1

Hydrogenation of C = O linkage 32

Experiment 11

Hydrogenation of C = O linkage 34

Experiment 111

Hydrogenation of Benzene Ring. 35

Experiment 1V

Selective Hydrogenation 37

Experiment V

Hydrogenation of a Bicyclic Hydrocarbon 39

Experiment V1

Reduction of Ethylene Linkage 39

Physical Properties 41

Relative Velocities 41

Mass Action 42

Operation 42

Analysis of Product 43

Experiment V11 44

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http://archive.org/details/catalytichydroge00leve

Page

Material 44

Operation 44

Analysis of Products 45

V. Conclusions 46

Vl. Bibliography 47

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June 1, 1916.

Harold Alvin Leroy

1 - Introduction.

Catalytic Hydrogenation of Organic Compounds.

Introduction.

The movement for the conservation of our resources has found its way into the oil industry. We cannot but observed that it has effected a shifting of the uses of various oils to those for which only the higher grades were formerly applied. For example, grades of oils formerly used in soap making, are now being consumed as edible products in the form of lard compounds, butter substitutes and the like; while lower grades of oils have now found their way into the soap industry.

However, this shift came only as a result of noteworthy developments in the refining of those oils and thus satisfactorily adapting them to these new uses. Among the most important of these are the many satisfactory methods for deodorization and decolorization, and more recently the process of hydrogenation or hardening of oils.

The conversion of olein, or olein containing oils into stearin has long been an ambition of the organic chemist. With such a process possible, relatively cheap oils could be converted into the hard fats needed in lard compounding and soap making.

As stearic acid is identical with oleic, except that it contains only two more hydrogen atoms, the problem seems apparently a simple one. However, on investigation it is found that oleic acid is exceeding resistant to the addition of this hydrogen, no matter how intimately they are mixed. But if a third substance is added in the form of certain suitable catalytic material, and

then these three intimately mixed at the proper temperature, the hydrogen will be readily absorbed by the oil, with the resulting conversion of the olein into stearin.

The hydrogenation process does even more than the early chemists ever anticipated. Even the most mal-odorous fish oils yield to this treatment and lose every trace of both their fishy odor and taste. And the darker grades of certain oils are partially bleached by this process. Further, it destroys traces of certain unsaturated substances thought to be slightly toxic in nature, thus rendering the same better adapted for human consumption.

While the process is conducted with more or less success by several manufacturers here and abroad, yet the important facts necessary for satisfactorily performing this operation are not generally known, but are retained as trade secrets. The patent literature on this subject is voluminous, but has for its prime purpose protection, rather than a specific record of the necessary information. It contains only broad statements and generalities, which usually results in the necessary repetition of all the experimental work supposedly performed by the patentee, if it is desired to conduct such a process.

Though the scientific literature contains much valuable information regarding the catalytic hydrogenation of organic compounds in general, still the treatment on the subject of the catalytic hydrogenation of the ordinary oils of commerce, is exceedingly meagre.

It has been the purpose of the writer to study the

catalytic hydrogenation of such compounds by means of a systematic investigation of the catalytic reduction or saturation of the various kinds of linkages, with several forms of catalytic material, and at different temperatures. And finally, the designing, constructing, and operating of a model hydrogenation apparatus to so intermix oil, hydrogen and catalytic material, and so control the temperature, that the process can be performed in a minimum time, and with the least possible expenditure of energy.

11 - History

11 - History.

In 1823 Doberiner[1] discovered that when hydrogen and oxygen were passed over spongy platinum they would ignite to form water. Later, it was found that other of the rare metals possessed similar properties, and to different degrees. Liebig, Wohler and others studied these phenomena. Saytzeff[2] in 1871, working under Kolbe, succeeded in reducing nitro-benzene to aniline, by passing a mixture of the vapors of the former with hydrogen over palladium black.

The use of the base metals in catalytic reduction began with Mond,[3] who in 1888 found that on passing carbonic oxide or gaseous hydrocarbons over metallic nickel at a temperature of 350° to 400° or metallic cobalt at 400° to 450°, carbon was the ultimate reduction product. In 1896 Sabatier and Senderen began a study of catalysis, which has resulted in one of the most laudable classics in chemical literature.[4] They used nickel and a great variety of both base and rare metals as catalysers. They demonstrated the effectiveness of nickel and other metals as carriers of hydrogen, and showed the reaction to be one of general application in the entire field of organic chemistry.

During the first decade of their study, all their reduction took place while the reacting substances were in the gaseous state. As the fatty glycerides are not volatile under ordinary pressures the above workers made no attempt to hydrogenate them.

Leprince and Sirche[5] were the first to attain success in

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catalytic hydrogenation in the liquid state, and with the application of this process to fatty glycerides begins the development of the " oil hardening industry."

Owing to the limited success of the above process its rapid application was prevented. This was also due to the small amount of knowledge of the catalytic action, and other essentials necessary to its successful operation, together with its high cost, due to its undevelopment. Then, when it was conducted on a commercial basis, patent difficulties and litigation began and which has continued to the present, becoming more intense during the past few years. The future outlook of this phase of the industry is a sad one, especially in this country. Again, our Patent System seems to have had an effect almost counter to its purpose, i.e., instead of encouraging industrial development, it has put a damper on it. The industry is now, 1916, in such a condition as to be very uninviting to capital, for the prospective investor is first confronted with the difficulty, if not impossibility, of leasing, or obtaining on other terms, the use of patents covering a commercially successfully process for performing this operation. And second, as an only alternative, he may develop a process, and in so doing he would experience considerable difficulty in obtaining patents of any value, because of the only exceedingly narrow claims that are now being granted to applicants for patents in this field. This condition has necessarily resulted from the granting of broad and sometimes even basic claims to applicants for commercially impractical and in many cases untried processes. The new worker will find that

it is well nigh impossible to work out a satisfactory process that isn't included in someone's claims already granted- so prolific are the patents in this field. Yet but little information of any real value can be obtained from the specifications of these patents. As a result many of these patents have been branded invalid, due to incomplete specification, and many more are doomed to fall in this same category. In any case, these prospects do not appear promising to the possible entrant to this industry.

A very limited number of concerns were hydrogenating oils prior to 1910, and these few were in Germany and had only a very small output. At this time plants were established in England and Holland, and in the following year in America. The industry has since grown to such a size as to occupy a very prominent position in the field of oil refining.

As the difference in price between the raw and finished product is small, and the cost of conducting the process relatively high, the margin of profit per pound or gallon is very small. This has resulted in the process being conducted on a large scale, so that there are only a small number of large plants converting an unknown amount of relatively low grade animal and vegetable oils into semi-fluid ond solid fats.

The history of the subsequent development is seen in the patent literature. It consists essentially of ways and means for continuous intimate mixture of oil, hydrogen and catalyser, its purpose being to effect more complete hydrogenation, as well as to reduce the time required. Much work has also been done in

the preparing of a more active and permanent catalyser, as well as apparatus for the preparation, resinification and testing of same.

The developments have taken place in many directions. Various workers operating under pressures of from 0.5 atmosphere to 15 atmospheres and temperature variations from 80° to 250°C.

A great variety of catalytic material has been used. Palladium has been found to be the most active, but its price has made its application to oil hydrogenation prohibitive. Nickel is by far the most active of the base metals and in its various forms is used to the exclusion of all other metals, in this work. Its several oxides and a large number of its salts have been used. The carbonyl is a source of obtaining the metal in a very finely divided form and while very active its life is shortened due to its increased seceptibility to "poisoners". This together with its difficulty of complete removal from the oil has prevented its extensive use.

Many forms of catalyser carrying material have been used, most common among these are: pumice, keiselguhr or infusorial earth, charcoal, bone black, saw dust, unglazed porcelain and the like, varying in size from that of a nut to an impalpable powder.

The tendencies of present developments in oil hydrogenation, seems to be essentially catalytic, with nickel in the metallic form as the catalyst. Pressures only sufficiently above atmosphere to pass through the column of oil, or to be used as an agitant, are becoming common practice. With the increase in the activity of the catalyst came the possibility of effecting the

reduction at a temperature just high enough to keep the oil sufficiently fluid to facilitate the operation. The time required for conversion has been reduced from days to a few hours, with promise of still greater shortening of time.

However catalytic reduction has many disadvantages. The hydrogen supply is still a difficult problem. The last trace of catalytic material remaining in the fat has to some extent prevented the wider use as a food. And the total cost of conducting the process is still high. So that some process is desirable in which the hydrogen would be generated in an active form in the oil itself and not requiring the use of catalytic material, thus making the process more direct and self-contained and resulting in a reduction of the cost, and the elimination of foreign material in the finished product. The electrolytic process appears to possess many of the above advantages and seems to be very promising.

And finally we have another illustrious example of how an understanding of chemical phenomena has changed the seemingly impossible of the last decade into the possible of this; and further, has resulted in the development of a vast industry having as its base this simple chemical reaction.

111 - Theory.

Theory.

General.

The phenomena at the base of these reactions is essentially one of catalysis, and the hydrogenation of oils another of its important industrial applications. The desideratum in reduction by means of hydrogen was to obtain it in a form that has been termed "nascent." This, like the term catalyser, has been sadly abused, and the seeming explanation of many chemical phenomena has rested under its cover. The term " nascent" was applied to hydrogen which had "just come into existence," and it was long thought that this was atomic hydrogen. But the fact that it possessed varying degrees of activity, depending upon its condition of formation, exploded this view.

It is usually considered as hydrogen which is liberated under conditions of varying amounts of free energy. As a reducing agent when formed under these conditions hydrogen is active whereas under ordinary conditions it would not be. The hydrogen can be made to possess this energy in many ways, and that obtained from each process will differ. Sufficient energy can be obtained in many forms of reduction by the mere addition of heat. Other reductions are so difficult that they cannot be made to take place unless the free hydrogen is generated in the mixture from electrolytic cells with electrode materials giving a maximum potential difference, or from suitable contact agents whose nature and form cause the hydrogen to be formed in the presence of this free energy.

In the realm of organic chemistry there are compounds

possessing these various gradations in difficulty of reduction and it has been shown by Sabatier and his co-workers that there are specific metals, when specially prepared, that are best suited to catalyse certain reduction in the presence of hydrogen.

Forms of Reduction.

These various forms of reductions may be classified according to the linkage between the atoms and also with regard to the kind of atoms thus linked. Certain metals have the characteristic properties of reducing the linkages between certain atoms and not others, and are thus used in selective reduction. Certain metals possess such great catalytic activity as to cause the hydrogen to be evolved under conditions of sufficient free energy, to completely reduce the substance to the hydrocarbon in one continuous operation and in some cases at moderately high temperatures to even split the hydrocarbon to two or more of a smaller number of carbon atoms. Then there are the less active materials which function so slowly that each intermediate step in the reduction may be isolated.

Relative Difficulty of Hydrogen Addition.

In this addition of hydrogen other factors come into play. The phenomena observed in the various forms of chemical reactions have their role here. The ethylene linkage(C = C) is more easily reduced than the peculiar unsaturation of the benzene ring. Ethylene is readily reduced in the presence of the less active catalytic material to ethane, which would not reduce benzene to cyclohexane. The unsaturated aliphatic acids of low

molecular weight are readily reduced to the corresponding saturated acids under conditions which would not reduce benzoic acid. The higher members of the series are not reduced as rapidly as the lower members. The difficulty of reduction by this method increases according to the order of the compounds in the following series: Aliphatic aldehydes, aromatic aldehydes, aliphatic ketones aromatic ketones, the ethylene linkage and finally the peculiar linkage of the benzene ring. Only reduction involving the fixation of hydrogen by addition to molecules where the double bonds exist, have been considered.

Phases of Material Hydrogenated.

As the rate of chemical reaction is a function of the degree of dispersion of the reacting substances, it at once becomes evident that this condition can be most effectively obtained when the reacting substances are in the gaseous phase. It was the difficulty of obtaining many substances in this form that prevented the earlier workers from hydrogenating oils and other non-volatile compounds. However, it has been known that a high degree of dispersion can be attained by the solubility of the gas in the liquid and that hydrogenation can be aided very materially by means of suitable catalytic agents which when carried on materials possessing high occlusive powers, like charcoal. Such material still further aids in effecting this dispersion by acting as carriers and reservoirs of hydrogen and giving it up to the oil as the hydrogen becomes chemically combined. With the aid of these agencies hydrogenation of liquids has been effected rapidly and hydrogenation shown to be of general application.

Catalysers.

The omnipotent factor in all these hydrogenation processes is the catalyser. The rate of reaction varies with its virility to a greater extent than to all other controlling factors.

Forms of Catalysers.

Catalysers used in hydrogenation processes are metals, their oxides and salts, and in the case of nickel the carbonyl. Both noble and base metals can be used. Palladium is recognized as the most active catalyst used in this form of reduction. Nickel is probably next in activity. Platinum, cobalt, copper and iron have also been used. Many of the base metals have been shown to possess no catalytic properties in effecting hydrogenation. In general the metals are the most active but the oxides closely approach them in activity. Many of the various oxides of a metal are present even when the metal is used as the catalyser and it is believed by some that the catalytic activity of the metal is due to such oxides. Others consider an equilibrium to exist, and the catalytic action to be the result of the shifting equilibria. Many salts have been used, mostly of nickel; in the form of the formate, acetate, lactate and oleate. Various workers have studied catalysers in this form, but in few cases has it been shown to be as active as the metals or the oxides. It is stated by Bedford and Erdmann[6] that salts are broken up into the oxides and even to the metals at the high temperatures required for hydrogenation with them as catalyst. Wimmer[7] on the other hand affirms that these salts are not reduced during hydrogenation.

In the case of the oxides, it is believed by many that they only catalyze when reduced to the metal. However, the work of Ipatiew and subsequently Erdmann[8] and Senderens and Aboulene[9] show that the oxides are not reduced to metallic nickel but catalyze as oxides and are very effective as such. Ellis[10] on the other hand believes that the presence of small traces of the metal are necessary, and that it is the mixture of metal and oxide that is effective.

Relative Advantages.

The advantages of the metals as catalysers are their greater activity and that the reaction may take place under ordinary pressures and moderate temperatures. However, they are exceedingly sensitive and are quickly poisoned by the most minute amount of H_2S, PH_3, AsH_3 and all the halogens. Their preparation is also more difficult and expensive.

Regarding the oxides of nickel, Senderens and Aboulene[9] concluded from their study that these oxides appear incapable of hydrogenation of organic material in the gaseous phase, but when used with liquids have an activity which cannot be attributed to the presence of the metal, and catalyse whatever their degree of oxidation. Certain reactions will take place with the oxides which will not proceed by the use of the metal. (This is probably due to the fact that the metal is so easily poisoned). The oxides are not very active except at high temperatures and pressures. They are however less susceptible to poisons and are more easily prepared.

The activity of the catalyst is also dependent on the

method of preparation. The experiments of Neigen and Bartels[11] indicate that the nickel reduced from the carbonate is somewhat more active than that from the oxide and far more sensitive than the material obtained on ignition of the nitrate. Other methods of obtaining the nickel in a finely divided state have been used. The most common of these is the nickel carbonyl. Nearly colloidal solutions of nickel have been prepared from solutions of the various organic nickel salts.

A noteworthy method of preparation of metallic nickel as a catalyst, is the process of Hagemann and Baskerville[12] which consists in electrolytically depositing nickel from a solution of a nickel salt, in the form of a very thin film, which is removed and crumbled and activated with hydrogen after being first oxidized by heating to 300° in air and then reducing with hydrogen at this temperature. These minute flakes are suspended in the oil. It is claimed that they are more effective as a catalyst than the material supported on a carrier, as they present both of their sides for action while the material supported on carriers presents only one active side. The form of the material facilitates its removal more readily than other forms.

Action of Catalysers.

The mechanism of the chemistry of this addition of hydrogen by means of catalysers is, like most other catalytic reactions yet unknown. Many hypotheses have been advanced by the various workers in this field, but they have thus far been unable to obtain experimental confirmation of their beliefs.

Sabatier,[13] who has done such extensive work with

catalytic nickel, believes the reaction to be due to the formation of metallic hydrides. The hydrogen first combining with the metal to form these hydrides on its surface. These compounds then react with the unsaturated compounds and being such active reducing agents break down liberating hydrogen in this energetic form, which then adds to the unsaturated substances. The metallic nickels thus formed is again acted upon by more hydrogen and the hydride again formed and the cycle repeated.

The various degrees of activity of nickel have been supposed to be due to the several hydrides which form as a result of the reduction of the metal from the oxides at various temperatures. The perhydride, H - Ni - H is supposed to form from nickel reduced below 270°, while the lower hydride, H - Ni = Ni - H, is probably formed from nickel reduced above 325°C, or from nickel that has been slightly poisoned. The perhydride is so virile as to rapidly hydrogenate the benzene ring, while the subhydirde will only reduce the ethylene linkages. Analogous reactions probably take place with the other catalytically active metals. It has been shown that in the case of nickel alone that various degrees of activity are capable of effecting only specific reductions. It is this fact that lead Sabatier to believe the existence of these several hydrides. Nickel obtained from the reduction of the chloride, and from the oxide at nearly 400°C has been shown to form only the suboxide, and capable of only mild reduction. Nickel formed from the oxide, prepared from the nitrate at the lower temperature is capable of reducing the stable linkage of the aromatic ring.

A hypothesis has been advanced by Erdmann[14] in which he offers an explanation of the role played by the nickel oxide as catalysers. The $Ni\overset{O}{<}Ni$ is supposed to add hydrogen with the formation of H - Ni - O - Ni - H. This in turn adds to the unsaturation in this manner,

$$-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Ni-O-Ni-H}{C}}- \quad \text{to} \quad -\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}- \quad \text{and} \quad Ni\overset{O}{<}Ni$$

and the cycle repeated. In the reactions involving the formation of Ni = O, the hydrogen is formed from the decomposition of the water thus,

$$Ni_2O + H_2O = 2NiO + H_2$$

With this in view it has been found desirable by Nicolet[15] and others, that hydrogen containing an appreciable moisture content facilitated reduction with the use of the nickel oxides.

Carriers.

The functions of the carriers are many fold. They were used as a lump material on which to deposit the catalytic agent. This formed a porous bed through which hydrogen, and the substance to be reduced, passed while in the gaseous phase. In the hydrogenation of liquids, carriers were used on which to deposit the catalytic material, in this case the powdered form. It was added here with the idea in view of facilitating the separation of the catalyst from the reduced liquid.

It has subsequently been demonstrated that certain material used as carriers, in the physical sense, in addition play an important role as an auxiliary material in the reduction. Substances having high occlusive power for hydrogen are desirable

for this purpose. Their function seems to be that of a hydrogen reservoir which it gives up to the catalyser as required. In the case of some material used as carriers, direct adsorption phenomena take place on its surface. With the use of certain substances for carriers, as keiselguhr a material reduction in the temperature of hydrogenation is effected.

Ellis[16] recommends the use of wood charcoal which possesses the property of absorbing or occluding hydrogen. Infusorial earth, pumice, amorphous silica have also been used.

Relation of Occlusion to Catalysis.

It was pointed out by Sievert and Krumhaar[17] that certain metals,e.g. cadmium, thallium, zinc, lead, bismuth, tin, antimony and others which possessed the property of occluding only traces of hydrogen, did not catalyse hydrogenation. On the other hand most metals that had the capacity of occluding appreciable quantities of hydrogen were effective as catalysers. And with some exceptions its activity was a function of this property. The occlusive power ofmetals vary materially with the physical form as well as the temperature. Palladium has the greatest occlusive power for hydrogen and is also the most active catalyser. The occlusive properties of various metals under normal conditions are shown in the following table, the values being the number of volumes of hydrogen absorbed by one volume of the metal.[18]

Palladium black	$17\text{-}18 \times 10^4$
Palladium leaf	830
Platinum leaf	3.8
Gold, precipitated	37-46

Gold leaf	0.48
Cobalt, reduced	59-153
Nickel, reduced	17-18
Iron, reduced	9.4-19.2
Iron wire	0.46
Iron, cast	0.57-0.80
Copper, reduced	0.6 - 4.8
Copper, wire	0.3
Aluminium, leaf	1.1 - 2.7

Certain metals having high occlusive powers may not be useful as catalysers due to their sensitiveness to poisons. From the results of the various workers in this field, it appears that the catalytic hydrogenation is a phenomenon which takes place as a result of local adsorption.

IV - Experimentation.

IV - Experimentation.

Apparatus.

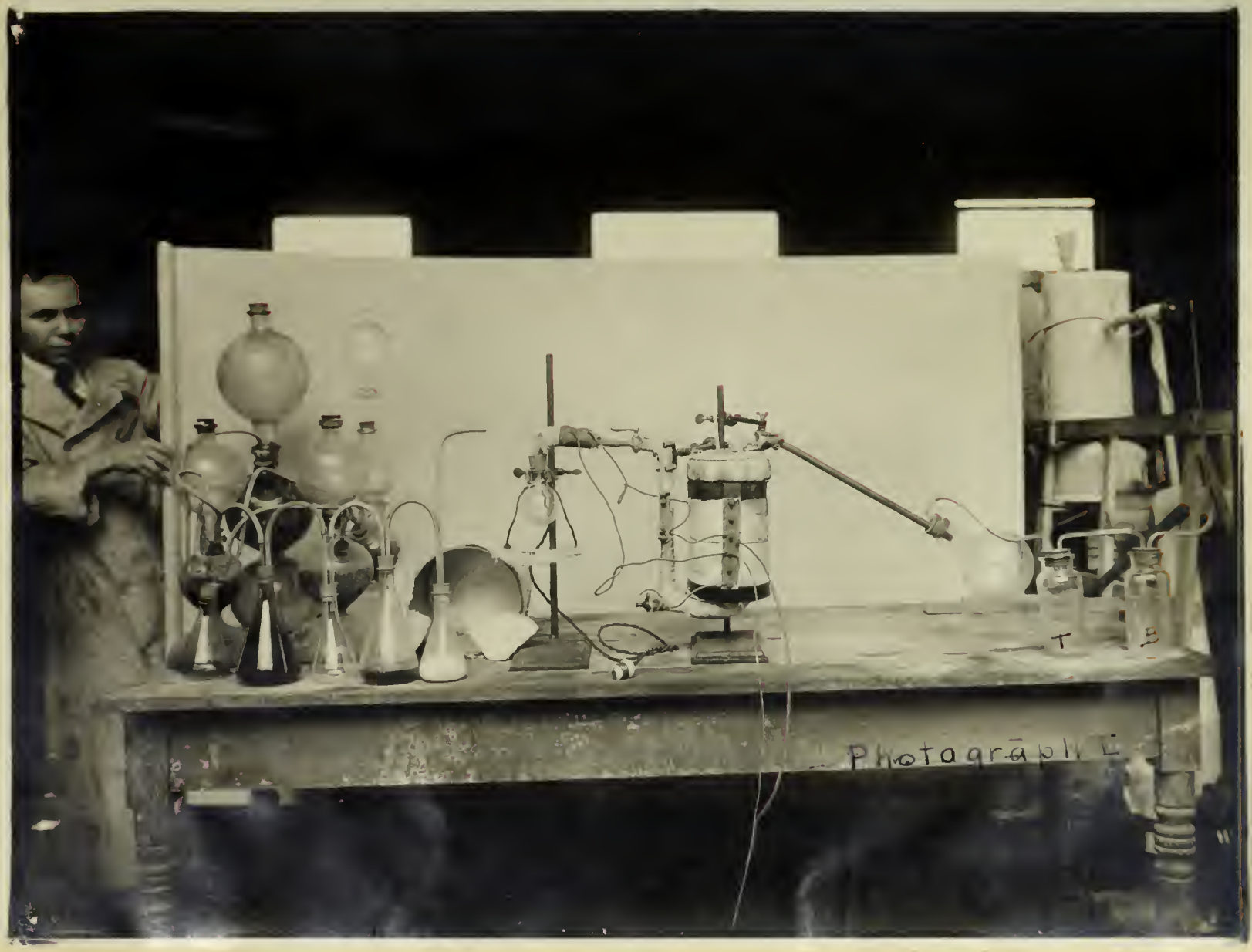
Since the nature of these reactions required the maintainance of uniform temperatures over a vast range, together with the need of mixing and preheating of the reacting gases and cause then to pass through a suspended mass of catalytic material, they demanded the construction of especially designed apparatus to perform these functions.

Small Apparatus.

The first apparatus built was designed primarily to be used for the hydrogenation of non-volatile liquids like the heavier fatty glycerides, but by using a separate vessel in which volatile liquids could be distilled or evaporated by means of a rapid flow of dry hydrogen, the apparatus became well suited to the reduction of any substance in the gaseous phase. Solids were also vaporized from this vessel, but if the hydrogenated product was a solid at ordinary temperatures, it usually deposited in the condenser tube and had to be melted out by the application of a Bunsen flame.

Large Apparatus.

The second apparatus was designed to permit of hydrogenation of oils at high temperatures, with facilities for close temperature regulation and control, as well as for hydrogenation at moderate pressures and reduced pressures; also for the activation of lump catalytic material. In addition the apparatus can be used for aeration, deodorization and decoloration of oils or

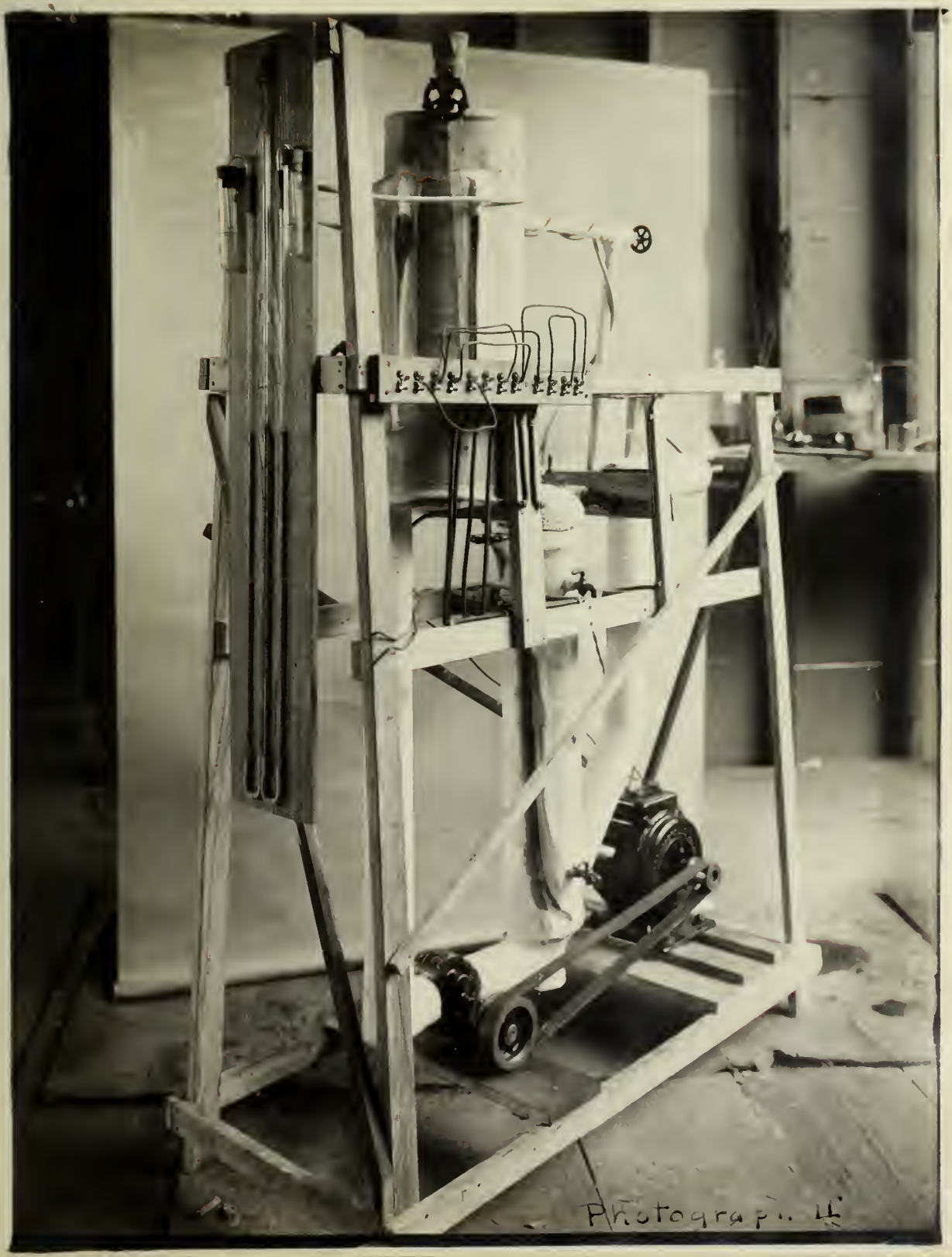

Photograph E

like substances.

Hydrogen Supply.

All the hydrogen used was obtained from Kipp generators using zinc or iron granules and dilute sulphuric acid. In connection with the small apparatus two or more generators containing a kilogram of zinc and 1200 cc of 20% sulphuric acid were used. For runs of eight hours or more four generators were used. To supply hydrogen in sufficient quantity at the required rate and necessary pressure, a generator was built operating on the Kipps principle. This consisted of two standard eleven gallon acid carboys and a two gallon aspirator bottle arranged as shown on drawing (11) and on photographs, (11, 111, and 1V). The piping consisted of 10 mm glass and rubber tubing and connected as indicated. Rubber stoppers were used throughout the generating system, and every stopper was securely fastened with wire to the neck of the bottle. The rubber tubing was fastened to the glass tubing by means of wire. The dilute sulphuric acid was prepared by mixing ten gallons of water and two gallons of concentrated (66° Baume) sulphuric acid. The aspirator bottle contained 35 pounds of cast iron turnings. A small piece of glass wool was placed in the lower neck of this bottle to prevent small pieces of iron from being carried into the acid bottle.

The hydrogen then passed into a second aspirator bottle. This served two functions; first, causing the velocity of the gas to be so reduced as to deposit suspended matter, both liquid and solid, thus acting as a trap; and second as a gas reservoir or



Photograph 11

gasometer. Its lower neck was connected with that of a third aspirator bottle by means of tubing containing a cock. Should an excess of gas be generated, the water would be forced from one bottle to the other until the head of water was equal to the gas pressure. As the pressure of the gas from the generator was greater than the head of water that could be obtained from these bottles, the pressure was reduced by means of a cock on the tube connecting generator with gasometer. As a safe guard against the loss of any hydrogen a cock was placed on the pipe connecting the two bottles forming the gasometer. This cock was closed as soon as the water was nearly emptied from one bottle thus preventing the gas from forcing all the water into one bottle and then through same and escaping into the atmosphere. Even with this valve closed this bottle acted as a satisfactory gas reservoir, as the compression of this large volume of gas was sufficient to cause a practically uniform gas flow through the hydrogenating apparatus.

The gas passed from this bottle through the purifying apparatus. This consisted of: first, a 10% solution of silver nitrate which removed H_2S, PH_3 and $CH \equiv CH$ (and AsH_3 when using Zn) second, a 10% solution of potassium permanganate which removed any unsaturated organic matter that may be present; and third, concentrated sulphuric acid which removed the major part of the moisture. After passing through this train the gas was practically pure and dry. It was tested by passing a portion through a fresh solution of silver nitrate and no precipitate was formed. The wash bottles were tall cylinders containing 300 cc of liquid. The

Photograph 22

gas passed into the liquid through 4 holes, 1 mm in diameter, and passed through 6 cc of liquid. The pure hydrogen then passed through a 5 mm glass tube 6 feet long connecting hydrogen generator with hydrogenating apparatus. The gas purification train for the small apparatus consisted of a common trap bottle (T), see photograph (1), potassium permanganate bottle (K), moisture separator (M), concentrated sulphuric acid (H) and calcium chloride(C). It was necessary that the gas used by the small apparatus be dry as possible, in order that it may evaporate a large amount of the compound.

Hydrogenating Apparatus.

In the hydrogenation of all the volatile compounds, the apparatus shown on photograph (1) and in section on drawing (1) was used. This consisted of a distilling flask, the converter and a receiver flask.

Construction of Apparatus.

Distilling Flask.

The distilling flask consisted of a short neck 100 cc round bottom flask carefully fitted with a cork stopper made gas tight and containing a glass tube reaching to the bottom of the flask and ending in a nozzle with a hole 1.5 to 2 mm in diameter; also a 360° thermometer having its bulb near the bottom of the flask, and an outlet tube leading to the converter. This was 6 mm inside diameter and made of thin brass. It was covered with a single layer of asbestos paper and over this was wound 24 inches of No. 30, B and S Gage Nichrome wire, then six layers of sheet

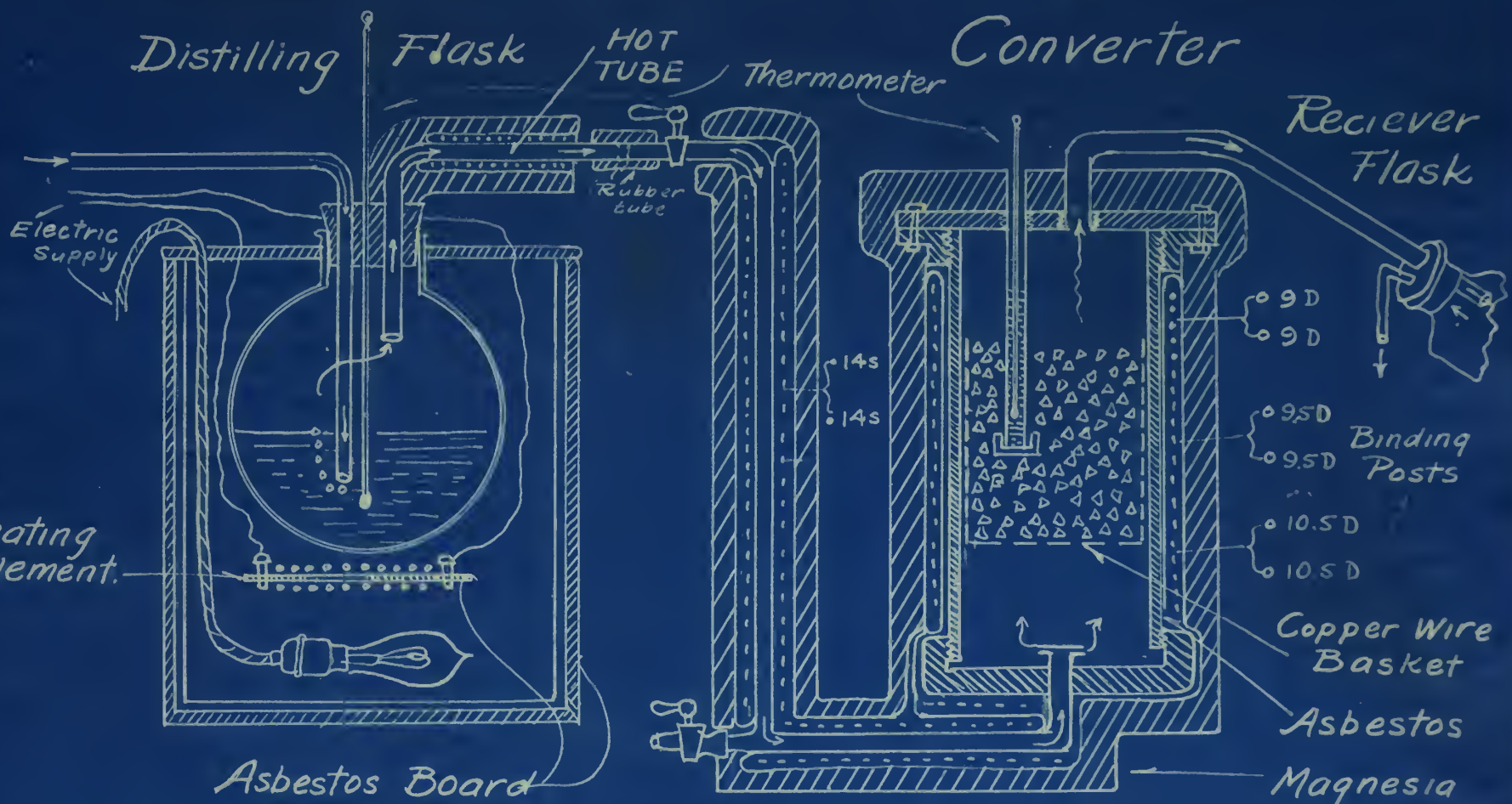
Photograph IV

asbestos and then bound with cloth. The terminals were brought out and fastened to 18" of No. 16 flexible cord and a layer of friction tape wound around the whole. It is designated as "Hot Tube" on photograph (1) and drawing (1). The flask is heated by means of a heating element made of a circular piece of asbestos board 4 mm thick, 12 cm in diameter and having a 6 cm circular hole cut concentrically in same. It is wound as shown with 9 feet of No.30 Nichrome wire, the terminals being connected to binding posts to which are also connected the leading in wires. Temperatures of nearly 250°C can be obtained in the flask in about 20 minutes. When temperatures up to 50° were to be maintained a 10 C.P. carbon incandescent lamp supplied the heat, and was arranged as shown. The flask and heating elements were enclosed by a cylindrical sheet iron vessel which was completely covered with a layer of $\frac{1}{4}$" asbestos board.

Construction of Small Converter.

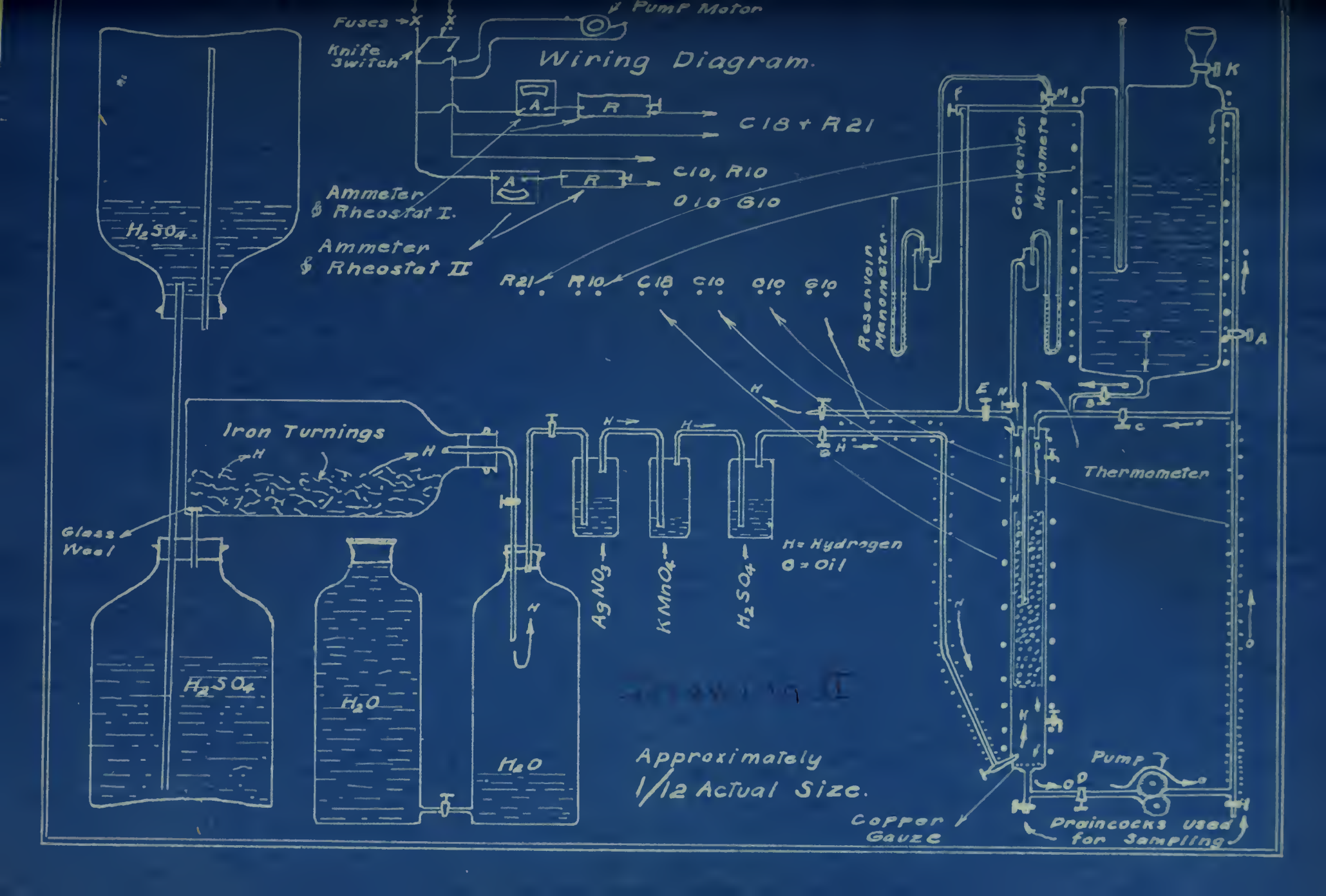
The converter is made entirely from standard pipe and pipe fittings. The shell is a 2 inch pipe 8 inches long, on the bottom is a 2 inch pipe cap with a hole in its center carrying an 1/8 inch pipe running through same and ending in an 1/8 inch cap having 4 one mm holes drilled diammetrically around its sides, thus diffusing the gas better than a single verticle hole and also preventing the passage of solid material into the gas pipe, as these holes are above the bottom of the 2 inch pipe cap. The incoming gas is led through a 1/8 inch pipe containing admission cocks at the two point indicated. The upper one is used for the incoming gas and the lower one for the drainage of liquid from converter and also to fill same / while the

Sectional Elevation of Small Hydrogen Apparatus



$\frac{3}{8}$ Actual Size
(Approximately)

gas is flowing. The rapid passage of the gas passed this lower cock tends to draw the oil into the converter, and greatly facilitates the filling of same. The top of the shell is fitted with a 2 inch pipe flange and this with a 2 inch blank flange plate in which was drilled two holes for 3/8 inch pipes. In one was fitted a 3/8 inch pipe 5 inches long and on the end of which was a 3/8 inch cap. This projected below the converter and was filled with mercury which surround a 360° thermometer. This indicated the average temperature of a large volume of the contents of the converter. In the second hole was fitted another 3/8 inch pipe which lead the gases out of the converter and acted as an efficient air condenser, the end section of which was arranged to have a slope of of 30° from the horizontal. The faces of the flanges were filed to a surface and then polished with fine emery. A gas tight joint was made by the use of Garlock asbestos packing No.900. All surfaces were covered with a layer of powdered Acheson graphite mixed with vaseline, which both assisted in making the joint gas tight and facilitated separation without sticking and destruction of the asbestos gasket. The shell, lower cap and incoming pipe line was covered with one layer of paper asbestos. A short piece of No.22 copper wire was arranged in a loop and bound around ends of the converter and pipe line and conducted the current from the binding posts to ends of resistance wire. Same also served to support the sheet asbestos while being wrapped with the resistance wire. All the sheet asbestos used was well moistened with water to facilitate its being formed to the contour of the vessel and piping. Three coils were wound in one layer on the shell of the converter.


Wiring Diagram.
Fuses
Knife Switch
Pump Motor
A
R
C18 + R21
C10, R10
O10 G10
Ammeter & Rheostat I.
Ammeter & Rheostat II
R21 R10 C18 C10 O10 G10
Reservoir Manometer.
Converter Manometer
K
F
M
A
B
C
E
N
H
Thermometer
Iron Turnings
Glass Wool
H_2SO_4
H_2O
$AgNO_3$
$KMnO_4$
H_2SO_4
H = Hydrogen
O = Oil
Approximately 1/12 Actual Size.
Pump
Copper Gauze
Draincocks used for Sampling

The wires were wound parallel and in the form of a helix with a gradual increase in pitch. As there was a larger amount of wire near the base, the temperature was higher, this tended to form convection currents in the oil and cause better mixing and diffusion of oil and gas. Two coils on the converter were wound with two strands of wire twisted together being equivalent to two coils in parallel or to a large size wire. Coil 9 D consisted of two 9 foot strands of No. 30 Nichrome wire; 9.5 D, two 9.5 foot strands of No. 30 and 10.5, one ten foot length of No. 30 wire; 14.5, one fourteen foot length of No. 30 wire wound on incoming gas pipe. Eight layers of sheet asbestos were wound around the gas pipe, and this covered with a piece of white cotton cloth. The wire on the converter was covered with three layers of sheet asbestos and this with a one inch layer of magnesia. This was fastened in position with copper wire and the whole wrapped with two layers of cotton cloth. The conductors were brought out to a board which contained the binding posts. This was fastened to the converter by means of two metal straps. A cover was made from asbestos board and readily removed. This reduced the radiation loss from the top of the converter. A copper wire basket 4 inches high carried the catalyst. It snugly fitted the inner wall of the converter preventing excessive passage of gas between it and walls of the converter.

The receiver flask consisted of a 1000 cc round bulb flask fitted with a rubber stopper connecting it with the condenser of the converter. The excess hydrogen after passing into this bulb was led into a trap bottle (T) photograph (1) to bottle (B)

which formed a water seal preventing the admission of air into the converter should the hydrogen supply fail.

Hydrogenation.

Construction of Large Apparatus.

The large hydrogenation apparatus consisted of two vessels, a converter and a reservoir, connected by means of suitable piping. The entire apparatus is made of standard pipe and pipe fittings. The reservoir is made of a 5 inch pipe 20 inches long fitted with a 5 inch cap on each end. The thermometer cup is made of 3/8 inch pipe and cap projecting 11 inches into the reservoir. It is provided with a 360° thermometer which is surrounded with mercury. This cap also contains an oil inlet consisting of a funnel and valve. The apparatus is filled with oil through this opening. An outlet pipe leads from the center of its bottom to the converter. The reservoir is heated by means of two coils, R 21 consisting of 21 feet of No. 20 nichrome wire and R 10, ten feet of No. 30 wire. The winding and insulation was constructed in the same manner as was the small apparatus already described.

The converter is made of a 1½ inch pipe 25 inches long fitted on the bottom with a 1½ inch pipe cap and on the top with a 1½ inch flange. The pipe cap contains the nozzle of the incoming gas pipe and also the oil outlet. A piece of 30 mesh copper wire gauze covers the bottom of the cap and prevents the passage of any small lumps that may fall out of the catalyser basket and thus prevent same from injuring the pump. The flange plate is equipped with a thermometer cup made from a 3/8 inch pipe, 10

inches long closed on one end with a 3/8 inch pipe cap. Same contains a 360° thermometer surrounded by mercury. This plate is also fitted to the 1/4 inch pipe carrying the incoming oil; a brass nozzle with a 3/32 inch hole in the same fits into the inside of this end of this pipe. A 1/4 inch outlet pipe is fitted to this plate and is used to carry off the excess of gas. The converter is heated by means of two coils; C 18 consisting of 18 feet of No. 30 B and S gage Nichrome wire and C 10, ten feet of No. 30 wire. The winding and insulation being of the same construction as the small apparatus already described. All the piping except the incoming gas pipe is made of 1/4 inch pipe. A pet cock is provided at the bottom of the converter to drain same and also to take samples of oil while the apparatus is in operation. A second pet cock is provided to drain the piping system and is also used for sampling. The drawing (1) and photograph (1) show the location of the various valves. Two open mercury manometers having a range from a vacuum to 2.3 atmospheres pressure are connected with the reservoir and the converter as shown. A safety tube is provided on each to prevent any mercury being drawn into the apparatus due to the sudden changes of pressure.

The incoming gas is preheated by means of coil G 10 consisting of 10 feet of No. 30 Nichrome wire wound around this 1/8 inch pipe in a manner as already described. The 1/4 inch oil pipe leading from the pump to the reservoir or converter is wound with 10 feet of No. 30 Nichrome wire and designated as coil (O) 10 and is used to reheat oil en route back to the reservoir or converter. The winding and insulation is constructed as already described.

The incoming gas enters the converter through a nozzle having a 1/16 inch hole. This gas stream leaving the nozzle is directed in such a way as to tend to churn the oil when the converter is partly full of the same. The nozzle enters the converter at an angle of 30° with the base and an angle of 60° with the radius at this point.

The oil is circulated by means of a rotary pump of the multi-vane cycloidal type, having a capacity of 0.75 gallon per 100 R.P.M. pumping against an oil pressure head of 4.2 feet and equipped with a relief valve set at 10 pounds. This pump is operated at a constant speed of 518 R.P.M being belt driven by a 1/8 H.P. single phase induction motor operating at 1150 R.P.M. The oil enters the reservoir near the top, thus preventing the oil from flowing back into the converter through the pump, and also causing the pump to operate under a constant pressure head of oil.

Operation.

Method 1.

The apparatus will treat varying amounts of oil. If a large quantity is to be treated the reservoir is filled through the funnel at the top. Valves A, B and D on drawing (11) on the oil system are opened and valve C closed. The oil then passes from the reservoir through the nozzle impounding on the catalyser in an atmosphere of hydrogen. It then trinkles through this material and passes out of the converter through valve D, then is pumped up through valve A and again enters the reservoir, and the cycle is repeated.

Method II.

A smaller amount of oil can be treated and the reservoir omitted from the cycle by closing valves A and B, and having only valves C and D open. The oil then travels through the converter, pump and portion of the oiling system.

Method III.

If a still smaller amount is to be treated, this may be admitted through the pet cock N, after removing the manometer connection, and the valves A,B,C, and D are closed and the pump not operated. The hydrogen then passes through this mass of oil as in the samll apparatus.

Preliminary Treatment of the Oil.

It is sometimes desirable to heat the oil and then blow hydrogen through so as to saturate the oil with it and drive out most of the oxygen dissolved before allowing the oil to come in contact with the catalyst. In order to do this it is only necessary to open valve B and close A, C, and D and by passing in hydrogen at G it will bubble through the oil after passing valve B.

Gas Piping System.

A gas pipe line, connecting the exhaust hydrogen supply with the reservoir was used to fill the space above the oil with an atmosphere of hydrogen. It was also used to apply a heavy pressure on the oil in the reservoir to quickly force the same into the converter. This was accomplished by having the hydrogen enter at J, close valve E, open F, and close K, A, C, D, and G. Then open

N, and remove manometer connection. On opening B the oil will pass from reservoir to the converter.

Electrical Heating System.

The wiring diagram is shown on drawing (11). The electrical energy used was an alternating current of 110 volts, 60 cycles, single phase. An ammeter with scale reading of 0 - 50 amperes was used on circuit I which supplied the current to coils C 18 and R 21. An average current value of about 4 amperes was required by each of these coils. This value could be obtained by connecting them in series. Circuit (11) contained an ammeter with scale reading 0 - 5 amperes and supplied coils C 10, R 10, O 10, and G 10. Carbon dish rheostats were used to regulate the current in each circuit. With the full voltage across their terminals coils C 10, R 10, O 10, and G 10 consumed 1.5 amperes per coil. The electric motor consumed 4 amperes.

Removable Container for Catalytic Material.

A brass tube whose outside diameter was slightly less than 1 1/2 inches was fitted at its base with small pieces of No. 10 mesh copper gauze. This cylindrical basket was 12 inches high and was filled with the catalyst. It was supported from the thermometer pipe by means of an adjustable collar to which it was connected by means of two pieces of wire. Thus the catalyst basket was removed with the top flange plate of the converter. Two 1/4 inch pipe unions were used to disconnect the two pipe lines fastened to this plate.

Catalysers.

In these experiments the catalysers used were nickel and copper in a very finely divided metallic form supported on lumps of infusorial earth of various sizes.

Preparation.

A weighed amount of nickel nitrate crystals ($Ni(NO_3)_2 6H_2O$) were dissolved in approximately an equal weight of water and this was then heated nearly to 80°C. Infusorial earth which showed no action on treatment with concentrated acid and alkali was used. This material was graded by means of sieves which sorted the various granules of a given size together. A known weight of one size was heated in a sheet iron crucible to about 150° C and then slowly dumped into an evaporating dish containing the hot solution of nickel nitrate. As the air and moisture had been largely driven from the pores of the infusorial earth by this present heating, on coming in contact with the liquid it rapidly draws the same into its pores. Any excess of water is then evaporated. If all the lumps have not been wetted, more water must be added until there is sufficient solution to have moistened all the lumps. This mass is then dried with constant stirring with a stout glass rod. It is then removed to a nickel or iron crucible and heated gradually with constant stirring while the water of crystallization and then the oxides of nitrogen are being driven off. It is then heated still further for about 15 minutes to make certain that all the nitrogen oxides have been removed. The temperature should now be between 375° and 400° C. The mass is now dumpped out upon a piece of sheet iron and allowed to cool. Each granule

should appear uniformly covered and of a greyish color.

Activation.

A weighed amount of the above material was placed in the apparatus, the quantity taken approximately filling the basket of the converter. The temperature is gradually raised to 280°. Water vapor begins to come off at 220°, and all the oxide is not completely reduced even at the high temperatures. A final temperature of 325°-335° is attained and then the material is allowed to cool slowly in a stream of hydrogen. The activated material must be kept in an atmosphere of hydrogen until used, or revivified at the same temperatures.

In the preparation of finely divided copper as a catalyser, copper nitrate, ($Cu(NO_3)_2.3H_2O$) was used and the procedure outlined for nickel followed. However, cupric oxide was reduced at a lower temperature, 200° to 250°. The catalytic material now has a rose color. Sabatier[19] recommends the reduction of the Cu at 180° and Holleman[20] 250° to 400°. It was found, however, that a more active material was obtained when the reduction temperature was between 200° and 220°C.

Experiment 1.

Hydrogenation of the >C = O linkage.

Reduction of acetone to isopropyl alcohol:- The method used was essentially that of Sabatier. .Catalytic copper was used as it is not desired to carry the reduction to the hydrocarbon, but in steps in order to isolate the alcohol. The copper catalyst was prepared as above described using 25 grams of $Cu(NO_3)_2 3H_2O$

per 100 grams of 3/16 inch size lump infusorial earth. 40 grams of this material were placed in the basket of the small converter. 50 cc of acetone were placed in the distilling flask. The catalyst was prepared the day before and efforts made to keep it in an atmosphere of hydrogen. To make certain of its reduction it was revivified at 220° for 70 minutes. Additional water vapor was given off at this time. Two 400 mm helical tube condensers were connected in series and through which the gases passed after leaving the receiver flask, which itself was surrounded with ice water. About 15 cc condensed in this flask. The temperature of the distilling flask was maintained at from 26° to 34°C. As the temperature fell, due to the evaporation of the liquid, heat was supplied by means of the heating element already described, the heat control being regulated by means of radiation. The temperature of the converter varied between 195° and 205°. The average rate of hydrogen flow was about 110 bubbles per minute. After all the liquid in the distilling flask was evaporated, which required 125 minutes, the converter temperature was raised to 250°C which drove out vapors occluded in the pores of the infusorial earth, and at the same time hot dry hydrogen passed through the converter. The yield was very small and this quantity was further reduced due to a portion having been evaporated by the passage of the hot dry hydrogen over the same.

The experiment was repeated under the same conditions with the following exceptions: the temperature of the converter was maintained at 185° with variation between 180°-190°. The distilling flask operated at a temperature of 7° to 10°. To pre-

vent a fall in temperature due to the loss of heat of vaporization of the acetone, a 16 C.P. incandescent lamp supplied the necessary heat. An ice water bath was maintained in both condensers and around the receiver flask. The gases after passing through the condensers were bubbled through toluene. 8 cc condensed in the receiver flask, 31 cc in container at bottom of the condensers, and 6 cc were obtained by fractionation from the toluene. These portions were mixed and treated successively with three portions of a saturated solution of $HNaSO_4$, the layers separated and the solution of $HNaSO_4$ extracted with ether and reclaimed 3 cc. The total yield of isopropyl alcohol after distillation was 11 cc, 21% of theoretical. B.P. = 80° - 82°. The small yield is due to this being an equilibrium reaction and proceeds in both directions simultaneously as stated by Sabatier.[21]

Experiment 11.

Hydrogenation of the >C = O Linkage.

Reduction of Benzaldehyde to Benzyl Alcohol: - The purpose of this experiment was to study the catalytic effect of finely divided copper and hydrogen as a reducing agent of aromatic aldehydes. A new and equal portion of the CuO on infusorial earth from the same batch was place in the basket of the converter. The copper was reduced at 200°-210° reaching a maximum temperature at 220° and required 4 1/4 hours before the copper was completely reduced and no water vapor be given off from the converter. The benzaldehyde was purified by treatment with dilute (1:10) KOH to remove benzoic acid and then distilled. 50 grams were placed in

the distilling flask and was vaporized by passing hydrogen through at a temperature of 155°-170°. The temperature of the converter varied from 180°-195°. The hydrogen flow was approximately 90-100 bubbles per minute. In 1 1/2 hours all the benzaldehyde had been passed through the converter. A temperature of 265° was reached in the converter and a rapid flow of hydrogen was passed through for 15 minutes before all the benzaldehyde and benzyl alcohol was removed from the converter. The product was treated three times with a saturated solution of $HNaSO_4$ to remove all the benzaldehyde, and the various $NaHSO_4$ solutions extracted with ether to reclaim any benzyl alcohol. The residue was then distilled at 200°-203° and a very small yield was obtained. The experiment was repeated under similar conditions with the following exceptions: the catalyst was revivified for 65 minutes. The distilling flask was maintained at a temperature of 110°-120° and the converter at 205°-220°. The hydrogen flow was increased to nearly 180 bubbles per minute. All the benzaldehyde had been vaporized from the distilling flask in 4 1/4 hours. 37 cc were obtained from the receiver flask and was purified as described above. This gave a yield of 19% and had a B.P. of 201°-203°. 1.5 cc of toluene boiling at 110-111° was also obtained- probably as a result of operating at higher tmeperature.

Experiment 111.

Hydrogenation of the Benzene Ring.

Reduction of benzene to cyclohexane: In general the method of Sabatier with modifications described by Noyes were

followed. The nickel catalyst was prepared as already described using 75 grams of $Ni(NO_3)_2.6H_2O$ and 50 grams of 3/16 inch lump infusorial earth. The small converter and distilling flask together with the condensing apparatus described in experiment 1 was used. The reduction of the nickel took place at 240° to 260° for 140 minutes and finally reaching a maximum of 290°. It was then allowed to remain in an atmosphere of hydrogen for 24 hours and again subjected to hydrogen flow and a temperature of 260° to 290°. 50 cc of benzene were evaporated in 175 minutes. The average rate of hydrogen flow was about 120 bubbles per minute. The distilling flask was operated at a temperature of from 33° to 35° C. heated by means of a 16 C.P incandescent lamp. The converter temperature varied from 182°- 192°C. 48.5 cc were collected from receiver flask,container at bottom of the condensers and what was reclained from alcohol solution. This was then put in a 100 cc dropping funnel which was placed at the top of a 500 mm condenser arranged for refluxing. A 300 cc round flask was connected to the bottom of the condenser, and contained 75 cc of 20% fuming sulphuric acid. The hydrocarbons were added drop by drop with vigorous shaking. After the reaction started the flask was placed in a bowl of water to keep it cool. Finally after all the product had been added the mixture was heated in a water bath for 100 minutes. After the flask had cooled, the contents were poured into a separatory funnel and the major portion of the cyclohexane removed. The acid layer was slowly poured into a large volume of ice water, this was then extracted with ether and the product reclaimed, after drying and evaporating the ether

was added to the large portion. This was again treated with a new portion of fuming sulphuric acid as above described. A small portion was tested with dimethyl sulphate and showed no diminution in volume. The product was finally dried with metallic sodium and distilled. B.P. was 80°-81°. A yield of 76% was obtained.

Experiment IV.

Selective Hydrogenation.

The Hydrogenation of aromatic linkages without reducing a hydroxyl group.

The Reduction of Phenol to Cyclohexanol.

Nickel catalyser prepared as above described was used. In the preparation equal weights of $Ni(NO_3)_2.6H_2O$ and 1/4 inch lump infusorial earth were thus treated. The procedure was essentially that of Sabatier and Senderen.[22] The catalyst was activated at 280° for 220 minutes reaching a final temperature of 272°. The phenol was evaporated at 120°-125°; 50 grams requiring 205 minutes. The converter was operated at a temperature of 150° reaching a maximum of 168°. The hydrogen flowed at the rate of about 150 bubbles per minute. At the end of the experiment the converter was heated to 250°C. and about 6 cc of liquid was condensed in the receiver flask. As the converter was operated at a temperature far below the boiling point of phenol, it is probable that the catalytic material separated out mechanically any suspended particles of phenol vapor. The phenol may also have condensed on the surfaces of the infusorial earth and then have been occluded by the same. It has also been suggested than an

intermediate compound of phenol and the catalyst may have formed that was broken up only at the higher temperatures. The product obtained was washed with dilute KOH (1:10) until the odor of phenol had disappeared and the residue was free from phenol as indicated by the $FeCl_3$ test in water. The product was dried and distilled. A small yield was obtained and it was thought that a large part of the product was lost in the purifying treatment. The pure cyclohexane obtained was studied. It was found to be very soluble in dilute KOH (1:10) and also (1:30) and very appreciably soluble in water. Thus the major part was not separated from the phenol.

The experiment was repeated and of the 50 grams of phenol placed in the distilling flask, 48 grams of the product were obtained. This was then treated with 150 cc, in three successive portions, of a dilute solution of KOH (1:10) which was saturated with K_2CO_3. This mixture was thoroughly shaken and after separation was extracted with ether, dried and evaporated and the small amount reclained added to the original which was again washed this time with a saturated solution of K_2CO_3. This product was then fractionally distilled and boiled at 160°- 161° giving a yield of 62%. This material was a water white liquid having no trace of phenol odor but rather that of the terpenes, and did not respond to the $FeCl_3$ test for phenol. 7% of the cyclohexane was obtained, same boiled at 81°C and was insoluble in dimethyl sulphate. This was probably formed when the converter was heated to 250° as at this temperature, according to Sabatier, both the ring and the hydroxyl group are reduced.

Experiment V.

Hydrogenation of a Bicyclic Hydrocarbon.

Reduction of Naphthalene to Decahydronaphthalene.

This substance had not been reduced by this method, the formation temperature was stated to be 230°.[23] A fresh portion of catalytic nickel from the same batch as that in the preceeding experiment was reduced under similar conditions. 50 grams of naphthalene was placed in the receiver flask. The distilling flask was operated at a temperature of about 160°C for 140 minutes. The converter temperature was maintained between 220° and 240°. Much difficulty was experienced with naphthalene crystals clogging up the condenser tube of the converter. These were periodically removed by heating the same with a Bunsen flame. The tubing connecting the receiver flask with the trap and wash bottles were also chocked with crystals. 35 grams of the product were obtained from the receiver flask. This was treated with 5% fuming sulphuric acid at room temperature. The entire mass seemed to have dissolved. The acid was diluted and extracted with ether which was dried and evaporated and 3 grams of a dark brown tarry substance remained.

Experiment VI.

Reduction of the Ethylene linkage, $>C = C<$

The hydrogenation of olein to stearin by means of Hydrogen and Catalytic nickel.[24]

The small apparatus already described was used. Four Kipp generators supplied the hydrogen. 35 grams of catalytic

material was placed in the basket in the converter. This material contained 6.5 grams of Ni_2O_3 and on activation reduced to 4.6 grams of metallic nickel. The 1.9 grams of oxygen reduced absorbed 0.5 gram of hydrogen forming 2.4 grams of water. The major part of the reduction took place at 290° to 300°. A maximum of 390° was reached (accidently). The rate of the hydrogen flow was about 140-160 bubbles per minute. The ratio of the catalytic nickel to oil was approximately 2.3%.

200 cc of Proctors and Gamble's refined Cottonseed oil was placed in the converter through the lower set cock after the activation of the catalyst as above described. As the constituent of the cottonseed oil under consideration is tri-oleic-glyceride, the reaction of the reduction of olein to stearin the tri-glyceride of stearic acid, may be represented as follows:

Olein ⟶ Stearin

$$\begin{array}{lll} CH_3(CH_2)_7CH=CH(CH_2)_7C(=O)O-CH_2 & & CH_3(CH_2)_{16}C(=O)O-CH_2 \\ CH_3(CH_2)_7CH=CH(CH_2)_7C(=O)O-CH & \xrightarrow[180^\circ]{3H_2} & CH_3(CH_2)_{16}C(=O)O-CH \\ CH(CH_2)_7CH=CH(CH_2)_7C(=O)O-CH_2 & & CH(CH_2)_{16}C(=O)O-CH_2 \end{array}$$

Cottonseed oil contains varying amounts of the glycerides palmitic, stearic, linolenic, linolic, and oleic acids. If it were all olein, or had a total unsaturation equivalent to pure olein, it would have an iodine number of 89.8. The degree of unsaturation of this oil was measured and found to have the iodine number of 118.6. The following comparative data is illuminating.

	Pure Olein	Proctor & Gamble's Cottonseed oil	On basis of Iodine No.= 100
Iodine Number	86.9	118.6	100
Gm. H_2/ gm.oil	0.00684	0.00934	0.00788
Liter H_2/1000gm oil	76.1	104	87.6
Liter H_2/liter oil	69.6	95.6	80.1
Lbs.H_2/ lb oil	0.00684	0.00934	0.00788
Cu.ft.H_2/ lb oil	1.215	1.670	1.399
Cu.ft.H_2/Cu.Ft oil	69.6	95.6	80.1

This table shows the amount of hydrogen absorbed for complete saturation. By dividing the values in column(111)by 100 the hydrogen absorbed per unit change in the iodine number is obtained.

Physical Properties.

Olein : Mol.Wt = 884.83; M.P = -50°; Sp.Gr. = 0.915 15°/15°

Stearin: Mol.wt.= 890.88; M.P = 71°; Sp.Gr. = 0.8621 80°/4°

Hydrogen : Mol.wt. = 2.016; Density = 0.08987 gms./liter.

Relative Velocities.

With the catalytic activity constant as well as the pressure, the temperature will determine the relative velocities of the reactions. In cottonseed oil which contains over 50% of linolic glyceride, the following reactions will be favored at their respective temperatures:-[15]

$$\underset{\text{Linolic glyceride}}{(CH_3(CH_2)_4CH = CH\ CH_2CH=CH(CH_2)_7COO)_3\ C_3H_5}$$

$$3H_2 + Ni \quad \Big| \quad 120^\circ$$

$$\downarrow$$

$$(CH_3(CH_2)_4CH = CH\ (CH_2)_{10}COO)_3\ C_3H_5$$

Iso-oleic glyceride

$$3H_2 + Ni \downarrow 120^\circ$$

$$(CH_3(CH_2)_{16}COO)_3\ C_3H_5$$

Stearic glyceride

While at the higher temperature this reaction is favored:-

$$(CH_3(CH_2)_4\ CH = CH\ CH_2CH = CH\ (CH_2)_7\ COO)_3C_3H_5$$

Linolic glyceride

$$3H_2 + Ni \downarrow 180^\circ$$

$$(CH_3(CH_2)_7CH = CH\ (CH_2)_7COO)_3C_3H_5$$

Oleic glyceride

$$3H_2 + Ni \downarrow 180^\circ C$$

$$(CH_3(CH_2)_{16}COO)_3C_3H_5$$

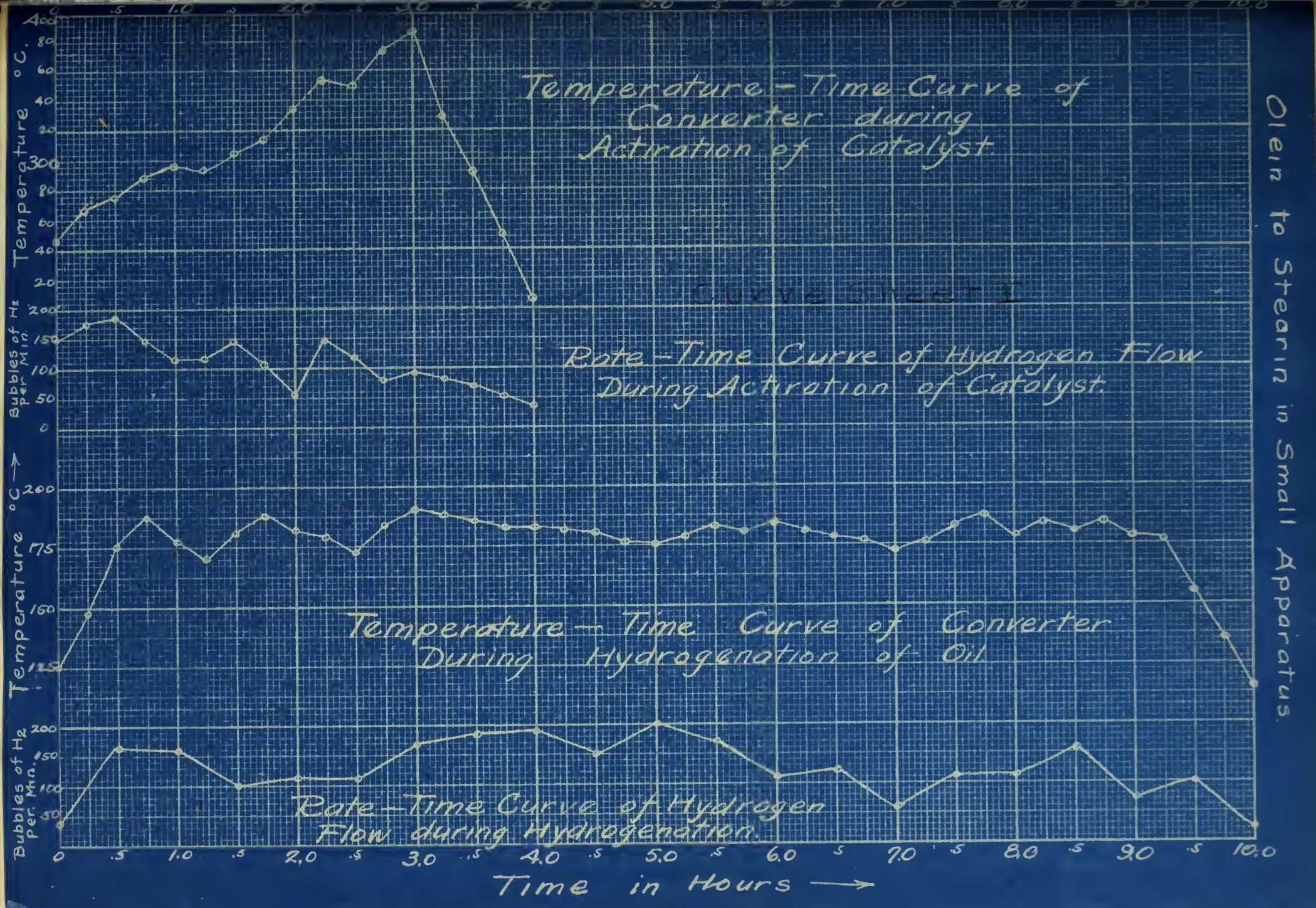
Stearic glyceride

Mass Action.

This reduction proceeds while the substance to be hydrogenated is in the liquid phase, the gas is bubbled through the oil; the hydrogen is kept in excess(of that absorbed) by passing it through the oil at a more rapid rate than it is absorbed, thus driving the reaction in the desired direction.

Operation.

Four Kipp's generators filled with zinc granules and 1:5) dilute commercial sulphuric acid supplied the hydrogen. The rate of hydrogen flow for both the activation of the catalyst and


Temperature – Time Curve of Converter during Activation of Catalyst.
Temperature °C.
Bubbles of H2 Per Min.
Rate – Time Curve of Hydrogen Flow During Activation of Catalyst.
Temperature °C →
Temperature – Time Curve of Converter During Hydrogenation of Oil
Bubbles of H2 per Min.
Rate – Time Curve of Hydrogen Flow during Hydrogenation.
Time in Hours →
Olein to Stearin in Small Apparatus.

the reduction of the oil is shown graphically on the curve sheet (1). The time required for activation as well as the time of hydrogenation is also indicated. Temperature readings of the converter were observed every five minutes, both during the reduction of the catalyst and the hydrogenation of the oil; their values are plotted as ordinates of both curves.

The pressure was practically that of the atmosphere, as there was sufficient pressure produced by the Kipp generators to force the gas through the cleaning apparatus, while the outlet was connected with a Venturi tube vacuum pump.

Analysis of Product:-

When the oil had reached a temperature of about 100°C it was poured into a hot water funnel containing two sheets of filter paper and a layer of bone black. This operation was repeated three times and removed practically all of the catalyst and suspended matter. The oil was now clear and of a yellow color somewhat darker than the original sample.

The degree of unsaturation of the partially reduced oil was measured by the Hanus Method. A Hanus Iodine solution and a (standard) sodium thiosulphate solution were prepared and standardized.[25] The untreated oil had an iodine number of 118.6 and the hydrogenated oil 72.6, which is a reduction of 38.8%. The titer value of the original oil was 35.1 and the hydrogenated oil 39.2. This product was a white tallow-like substance with an odor similar to lard.

Experiment. V11.

The Hydrogenation of Cottonseed Oil using the Large Apparatus described above.

In the preparation of the catalyst a small amount of the nickel salt was used because the lumps were larger thus presenting a smaller surface per unit weight.

Materials:-

100 grams of infusorial earth consisting of lumps 5/16 to 3/8 inch in diameter, on which was deposited 50 grams of $Ni(NO_3)_2.6H_2O$. 2000 cc of Proctor and Gamble's Refined Cottonseed oil was treated.

Operation.

Curve sheet (11) shows graphically the temperature variation with the time for both the reservoir and the converter. The catalyst was activated at 300°-325° for 3 1/2 hours and reached a maximum temperature of 380°C. The oil in the reservoir was heated to 80° and hydrogen blown through it for 15 minutes. When the converter temperature had reached 110° after the activation of the catalyst, the pressure of the hydrogen was applied to the oil in the reservoir, and the same was forced to fill the converter and piping system. This oil wetted the catalyst and prevented the reoxidation of the nickel. The apparatus remained in condition for 14 hours after which time the converter was reheated, the pump started and the hydrogen passed through the oil.

The total current curve on the curve sheet (11) shows the variation of the current with time. This represents the sum of the two ammeter readings which indicated the current intake of

the respective heating coils as described above.

The hydrogen pressure during activation was practically constant at 40 mm (785 mm absolute pressure). The hydrogen flow was sufficiently rapid to maintain this pressure. The hydrogen was supplied by a large Kipp generator as already described.

The catalytic material contained 14.15 grams of Ni_2O_3 which on reduction gave 10 grams of metallic nickel and required 0.52 gram or 4.67 liters of hydrogen to combine with the 4.15 grams of oxygen removed forming 4.67 grams of water. The ratio of nickel to oil was 1 to 184 or 0.544%

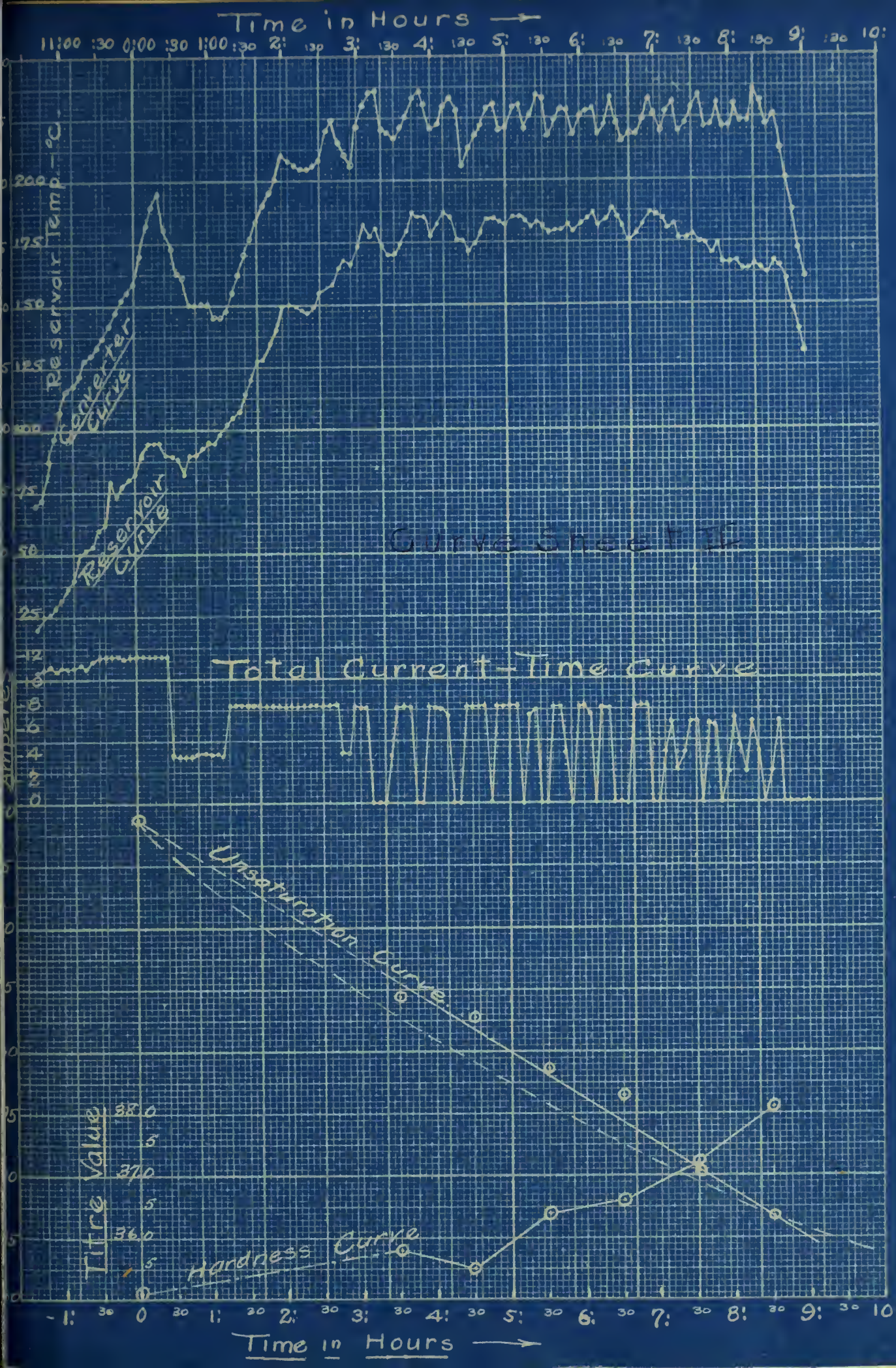
Samples were taken every hour after 3 1/2 hours of operation. These were obtained from the pet cock just after the oil passed through the pump.

The pressure in the reservoir during the hydrogenation remained practically constant between 35 mm and 40 mm (785 mm absolute), and that of the converter at 20 mm to 25 mm of mercury (770 mm). As the

As the pump was operated far below its capacity, the reservoir ccontained practically all the oil, which passed in a small stream from a 1/8 inch nozzle into the converter which was filled with hydrogen. The oil trinkled down through the bed of catalytic material and was kept in circulation by the pump as described above.

Analysis of Products.

The samples were heated and filtered as described in the preceeding experiment. Both the iodine number and the titer value of each sample was measured. The curves on curve sheet (11) show


Time in Hours →
11:00 :30 0:00 :30 1:00 :30 2: :30 3: :30 4: :30 5: :30 6: :30 7: :30 8: :30 9: :30 10:
Reservoir Temp. °C
200
175
150
125
100
75
50
25
Curve Sheet
Total Current-Time Curve
Amperes
12
10
8
6
4
2
0
Unsaturation Curve
Titre Value
38.0
5
37.0
5
36.0
5
Hardness Curve
-1: 30 0 30 1: 30 2: 30 3: 30 4: 30 5: 30 6: 30 7: 30 8: 30 9: 30 10:
Time in Hours →

these values graphically. The iodine curve shows the decrease in the degree of unsaturation with time; and the titre curve, the increase in titre value with time.

V - Conclusions.

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1. That the hydrogenation of aldehydes and ketones to their corresponding alcohols with reduced copper as catalyser is a reversible reaction, the equilibrium varying with the temperature.
2. That selective hydrogenation can be effectively conducted by the use of suitable catalysers at definite temperatures.
3. That reduced copper and hydrogen will reduce the carbonyl and hydroxyl groups, but does not affect the peculiar unsaturation of the benzene ring.
4. That nickel reduced at relatively low temperatures from the oxide prepared from the nitrate, will nearly quantitatively reduce benzene to cyclohexane.
5. That the hydrogenation of liquids can be effected as readily as gases with the aid of suitable catalytic material.
6. That certain material used as carriers of the catalytic agents are themselves accelerators in the reduction, and lowers the temperature necessary for the same.
7. That the activity of catalysers in the reduced metallic form is a function of their capacity for occluding hydrogen.
8. That the rate of hydrogenation of oil decreases with time.
9. That an apparatus has been built that has been used to hydrogenate organic compounds successfully in the liquid or gaseous phase.
10. That a model hydrogenating plant has been designed, built and operated and has shown its ability to hydrogenate fatty glycerides.

VI - Bibliography.

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